

Prototype Scale Development of an Environmentally Benign Yellow Smoke Hand-Held Signal Formulation Based on Solvent Yellow 33

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Supporting Information

ABSTRACT: We report herein the development of an environmentally benign yellow smoke formulation aimed to replace the environmentally hazardous mixture currently specified for the U.S. Army's M194 yellow smoke hand-held signal. Static ignition test measurements have identified a replacement candidate that generates a robust fountain of yellow smoke, burning for 15 s from a consolidated cardboard tube configuration. This new formulation meets the burn time parameters outlined in the military requirement and is composed entirely of dry, powdered, solid ingredients without the need for solvent-based binders. In addition, this formulation was found to have relatively low sensitivity to impact, friction, and electrostatic discharge.



"Mellow yellow."
A military hand-held signaling device is now "armed" with eco-friendly yellow smoke.

KEYWORDS: Hand-held signal, Solvent Yellow 33, Energetic materials, Pyrotechnics, Sustainable chemistry, Product life cycle management

INTRODUCTION

The energetic materials employed in many mission-critical U.S. military devices such as rockets, ammunition, signal flares, and training simulators contain once popular chemicals that are now scrutinized by environmental regulators.^{1–4} In order to prevent any compromise of mission readiness that may result from a ban ordered on such devices, there is an urgent need for new energetic formulations that do not contain any environmentally objectionable ingredients. To this end, environmentally sustainable formulations have recently been developed for a variety of pyrotechnic devices including flash bang grenade training simulators,⁵ colored illuminant signal flares,^{6–11} incendiary projectiles,¹² hand-held signal delay elements,¹³ and white smoke grenades.¹⁴ Aside from curbing chemical contamination during the life cycle of armaments, these efforts have directly benefitted training of U.S. military personnel. In 2010, for instance, the U.S. Army was permitted to resume training at Camp Edwards in Massachusetts (U.S.) with a perchlorate-free version of the M116A1 flash bang training simulator, once a 13-year-old administrative order was revised by the U.S. Environmental Protection Agency (EPA).¹⁵

While these developments offer encouragement for the U.S. military to overcome stringent environmental regulation, the list of ingredients targeted for elimination from energetic materials has been limited to potassium perchlorate, heavy metals (e.g., barium and hexavalent chromium),^{5–13} and phthalate-based binder systems such as Laminac 4116/

Lupersol.^{6–11,16} Here, we add to this list two toxic yellow dyes contained in the U.S. Army's M194 yellow smoke hand-held signal (HHS): benzanthrone and Vat Yellow 4 (Figure 1).

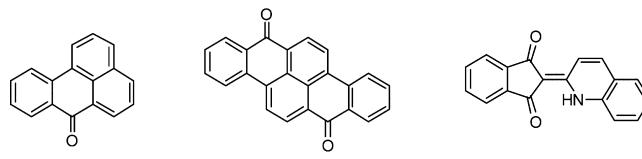


Figure 1. Chemical structures of yellow dyes.

Deployed during daytime close combat situations, the M194 is a tactical signaling device used to convey distress or troop location. As such, the chemical formulation in the M194 must be robust enough to produce the visual pyrotechnic effect without posing risk to the soldier or the environment. Moreover, the colored dyes must have low toxicity because they are a primary component of the formulation and are dispersed directly into the environment unconsumed by the key redox reaction.¹⁷

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Table 1. Makeup of In-Service M194, Yellow Smoke BES Control, and Formulation A

in-service M194		BES control		formulation A	
ingredients	wt %	ingredients	wt %	ingredients	wt %
Vat Yellow 4	13	Solvent Yellow 33	31	Solvent Yellow 33	31
KClO ₃	35	KClO ₃	29.5	KClO ₃	29.5
sucrose	20	sucrose	22	sucrose	22
NaHCO ₃	3	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	15.5	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	14.5
benzanthrone	28	stearic acid	1	stearic acid	1
VAAR	1	VAAR	1	NC	2

Production of the M194 yellow smoke HHS was discontinued during the early 1980s partly because of health concerns associated with benzanthrone and Vat Yellow 4. Both of these organic dyes pose serious hazards to human health and the ecosystem.^{18,19} In fact, Vat Yellow 4 is classified as a “Group 3” material by the International Agency for Research on Cancer (IARC) because the carcinogenicity of this compound remains undetermined.²⁰ In light of these toxicity issues and upcoming production demand for the M194 HHS, a program was initiated by the U.S. Army’s Armament Research, Development, and Engineering Center (ARDEC) to develop a replacement yellow smoke formulation containing an alternate nontoxic yellow dye: Solvent Yellow 33 (also called D&C Yellow No. 11) shown in Figure 1. This eco-friendly replacement dye has already gained widespread industrial use^{18,19} and has also been safely implemented in several Navy signaling devices.^{21,22}

EXPERIMENTAL SECTION

Materials. Potassium chlorate (MIL-P-150D, grade B, Class 7), sugar (MIL-AA-20135D, Type 1, Style C), sodium bicarbonate, and stearic acid were purchased from Hummel Croton, Inc. Solvent Yellow 33 (MIL-DTL-51485B(EA), Type II) was purchased from Nation Ford Chemical, Inc. Nitrocellulose (NC) was purchased from Alliant Techsystems, Inc. Vinyl alcohol acetate resin (VAAR) was purchased from McGean. Hydrated basic magnesium carbonate was obtained from Pine Bluff Arsenal (Pine Bluff, AR) and was confirmed to be Mg₅(CO₃)₄(OH)₂·4H₂O (hydromagnesite) by powder X-ray diffraction (XRD). Fumed silica (Cab-O-Sil M5) was obtained from Cabot Corp. All of the pyrotechnic pellets were encased in uncoated kraft cardboard tubes purchased from Security Signals, Inc.

Preparation of Yellow Smoke Formulations. After oven-drying the potassium chlorate overnight at 60 °C, formulations were prepared in 300 g batches by blending all ingredients according to their respective weight percentages. The control and formulations A–E (which contain solvent-based binders) were blended in a Hobart planetary air-driven mixer with an aluminum beater for 30 min, and each mixture was then transferred to a large ceramic dish. These formulations were oven-cured overnight at 60 °C prior to consolidation. Formulations F and G (which contain only dry powdered ingredients) were tumbled end-over-end in conductive plastic containers for 1 h and were ready for immediate consolidation without further processing.

The control and formulations A–G were weighed out in three 24 g increments and pressed into noncoated kraft cardboard tubes (length of 4.93 cm, inner diameter of 0.838 cm), with the aid of a tooling die and a hydraulic press, using a consolidation dead load of 5450 kg. The resulting pyrotechnic pellets contained 69.7–71.1 g of energetic material, and four pellets were prepared for each formulation. The top and inner core surfaces of each pellet were coated with a thin layer of thermite-based igniter slurry (composed of 33.0 wt % potassium nitrate, 24.5 wt % silicon, 20.8 wt % black iron oxide, 12.3 wt % aluminum, 3.8 wt % charcoal, and 5.6 wt % nitrocellulose in acetone), and a piece of quick match was horizontally placed across the top of the slurred surface. Pellets were remotely ignited with an electric match. Because of the inner-bored configuration of the pellets, the

burning propagation front migrated from the top down and inner core outward.

Characterization. A Malvern Morphologi G3S optical microscopy particle size analyzer was used to determine number-based CE diameter distributions. Powder XRD was carried out with a Rigaku Ultima III diffractometer with CuK α radiation (1.54 Å). The diffraction pattern was analyzed with JADE 7 software (Materials Data, Inc., Livermore, CA). Static ignition test data reflect averages from testing of four pellets per formulation. Burn times (seconds, s) were obtained from digital video recordings. Similarly, mass consumption rates (g/s) were calculated from these measured burn times and the weights of the consolidated pellets. Impact sensitivity tests were carried out according to NATO Standardization Agreement (STANAG) 4489²³ using a BAM drophammer. Friction sensitivity tests were carried out according to STANAG 4487²⁴ using a BAM friction tester. Electrostatic discharge sensitivity tests were carried out using an Albany Ballistic Laboratories electric spark generator.

RESULTS AND DISCUSSION

Table 1 details the environmentally hazardous formulation currently specified by the M194 technical data package. Although this formulation meets the military requirement of producing a dense visible yellow smoke cloud for 9–18 s, the total content of Vat Yellow 4 and benzanthrone equals 41 wt % of the entire formulation. With a 70 g pellet, this equates to a potential environmental exposure of approximately 29 g of the toxic yellow dyes throughout the life cycle of a single M194 signal! To mitigate this exposure, the development of an eco-friendly yellow smoke signaling formulation evolved from previous efforts in our group to develop an environmentally sustainable yellow smoke battlefield effects simulator (BES).^{18,19} In addition to sucrose and KClO₃ as the redox pair, the BES formulation consists of Solvent Yellow 33 as the smoke sublimating agent, hydrated basic magnesium carbonate (Mg₅(CO₃)₄(OH)₂·4H₂O) instead of sodium bicarbonate (NaHCO₃) as the endothermic coolant, stearic acid as the lubricant and processing aid, and vinyl alcohol acetate resin (VAAR) as the binder system (Table 1). Initial tolerance studies of the BES formulation and a discussion of the M194 system hardware were reported previously.^{18,19} We report here on how more extensive modifications to the BES formulation resulted in a new formulation that meets the M194 burning rate requirement.

As shown in Table 2, the BES control burned for 38.0 s, which is far from the range specified by the military requirement for the M194 (9–18 s). To shorten the burn

Table 2. Performance of Formulation A and BES Control

formulation	burn time (s)	burn rate (g s ⁻¹)
M194 military requirement	9–18	3.89–7.78
BES control	38.0	1.84
A	25.0	2.96

time, we employed the energetic nitrocellulose (NC) binder system to replace the nonenergetic VAAR binder system to produce formulation A (Table 1). Although further optimization was needed, this change profoundly shortened the burn time to 25.0 s, with a corresponding increase in the mass consumption rate (Table 2). While VAAR is not environmentally objectionable, this material is currently in short supply.²⁵ Thus, removing VAAR will also directly benefit the life cycle management of the M194 yellow smoke signal.

Coolant Studies. Having achieved a reduction in burn time, the tolerance of formulation A to further incremental changes was probed. The next adjustment was a reduction in the amount of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, which is an endothermic coolant and serves as a burn rate retardant and flame suppressant.^{26,27} Accordingly, coolant-lean formulations B and C were prepared with 5 and 10 wt % less $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ as shown in Table 3, and their

Table 3. Coolant-Lean Formulations B and C

formulation B		formulation C	
ingredients	wt %	ingredients	wt %
Solvent Yellow 33	36	Solvent Yellow 33	36
KClO ₃	29.5	KClO ₃	34.5
sucrose	22	sucrose	22
$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	10.5	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	5.5
stearic acid	1	stearic acid	1
NC	1	NC	1

Table 4. Performance of Coolant-Lean Formulations B and C

formulation	burn time (s)	burn rate (gs ⁻¹)
M194 military requirement	9–18	3.89–7.78
B	23.0	3.11
C	16.0	4.44

corresponding burn data are given in Table 4. The modest burn time improvement of 23.0 s exhibited by formulation B, containing 10.5 wt % $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$, can be attributed to the higher percentage of sublimable Solvent Yellow 33; the dye is a diluent and when more concentrated in a formulation, longer burn times will result.¹⁷ Also, the reduced amount of NC binder present in B can be expected to have a burn rate retarding effect because it is an energetic binder.²⁸ However, decreasing the coolant level by an additional 5 wt % with a corresponding increase in KClO₃ (formulation C) overrode both of these effects. Compared to A and B, formulation C gave a more drastically reduced burn time of 16.0 s, well within the M194 military requirement.

To better understand the relationship between coolant content and burn rate, formulations D and E were prepared, both of which are identical to B and C only using NaHCO₃ as an alternate coolant instead of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ (Table 5). As shown by the performance parameters for each in Table 6, incrementally reducing the amount of NaHCO₃ from 10.5 wt % (D) to 5.5 wt % (E) resulted in a dramatic reduction in burn time. However, both NaHCO₃-based formulations burned significantly longer than B and C, and neither was within the 9–18 s burn time specified by the military requirement (Table 6).

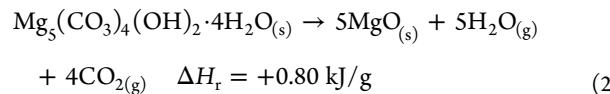
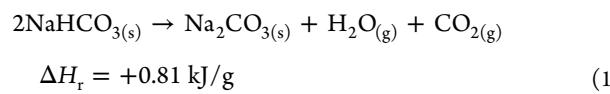
Table 5. NaHCO₃-Based Formulations D and E

formulation D		formulation E	
ingredients	wt %	ingredients	wt %
Solvent Yellow 33	36	Solvent Yellow 33	36
KClO ₃	29.5	KClO ₃	34.5
sucrose	22	sucrose	22
NaHCO ₃	10.5	NaHCO ₃	5.5
stearic acid	1	stearic acid	1
NC	1	NC	1

Table 6. Performance of NaHCO₃-Based Formulations D and E

formulation	burn time (s)	burn rate (gs ⁻¹)
M194 military requirement	9–18	3.89–7.78
D	49.0	1.45
E	24.0	3.02

The performance difference between hydromagnesite-based formulations (B and C) and their NaHCO₃-based counterparts (D and E) is explained by the different temperature ranges in which the thermal decompositions of these coolants occur. Although NaHCO₃ can decompose to Na₂CO₃, H₂O, and CO₂ (eq 1) within the temperature range at which sucrose/KClO₃-based smoke compositions operate (typically 200–400 °C),^{29,30} further decomposition of Na₂CO₃ to Na₂O and CO₂ does not occur in such compositions because of the much higher temperature required (800 °C).³¹ As for the thermal decomposition of hydromagnesite (eq 2), three steps have been proposed: first the loss of waters of crystallization, followed by decomposition of the hydroxide ions (also releasing water), and finally decomposition of the carbonate ions to release CO₂.²⁷ All three processes occur in the 200–550 °C range. Despite the fact that both are endothermic and have comparable per gram enthalpies,^{27,32} reaction 1 occurs completely within the cool-burning temperature range of sucrose/KClO₃ smoke compositions, whereas reaction 2 is incomplete.



Sodium bicarbonate is therefore a more aggressive coolant than hydromagnesite, as it effectively removes more energy from the smoke compositions in the temperature range in which they burn. As demonstrated by the results in Tables 4 and 6, the use of NaHCO₃ in place of $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ results in longer burn times (slower burn rates). Thus, employing $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ is essential to achieving a yellow smoke formulation that meets the short burn time requirement of the M194.

Final Adjustments. While useful in establishing relevant data points in our investigation, formulation C has the misfortune of containing NC that raises concerns for its long-term shelf life.³³ Although formulation C met the military requirement, NC-free formulations F and G were prepared and tested (Table 7) to avoid this technical aging risk. For both of these formulations, untreated fumed silica was introduced in the absence of a binder to promote homogeneity. To our

Table 7. NC-Free Formulations F and G

formulation F		formulation G	
ingredients	wt %	ingredients	wt %
Solvent Yellow 33	37	Solvent Yellow 33	40
KClO ₃	34.5	KClO ₃	34.5
sucrose	21.5	sucrose	21.5
Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	5.5	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	2.5
stearic acid	1	stearic acid	1
fumed silica	0.5	fumed silica	0.5

delight, formulation F gave performance slightly better than that of formulation C, burning for 15.0 s and well within the military specification (Table 8).

Table 8. Performance of Formulations F and G

formulation	burn time (s)	burn rate (gs ⁻¹)
military requirement	9–18	3.89–7.78
F	15.0	4.64
G	24.0	3.11

Recognizing a trend toward reduced burn times as the hydromagnesite content was decreased, we attempted to obtain an even shorter burn time with formulation G, consisting of only 2.5 wt % Mg₅(CO₃)₄(OH)₂·4H₂O. This, however, gave much longer burning smoke fountains of drastically reduced color quality. As shown in Figure 2, smoke fountains generated

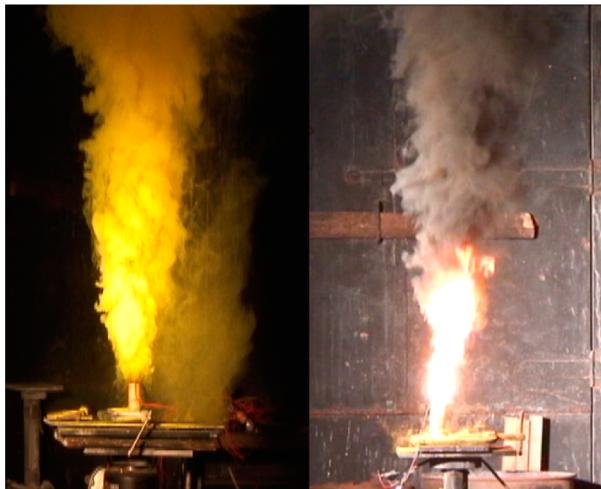


Figure 2. Images of smoke fountains generated by formulations F (left) and G (right).

upon burning of formulation F (left) exhibited excellent color quality, while formulation G (right) gave a fountain of primarily gray smoke with substantial incendiary effects. This is indicative of the oxidation of Solvent Yellow 33 that occurs when the reaction temperature is too high. Apparently, the hydromagnesite level in formulation G was too low to moderate the reaction temperature and to suppress flaming.^{26,27}

Sensitivity Testing. Having identified a lower boundary for the hydromagnesite content, it became clear that additional development would not lead to substantially improved performance beyond that exhibited by formulation F. Thus, the next step in transitioning formulation F to demonstration in full-up system hardware was to measure its sensitivity to various

ignition stimuli (e.g., impact, friction, and electrostatic discharge). Because the baseline M194 formulation was never prepared nor tested due to its aforementioned environmental and human health concerns, the sensitivity of formulation F was compared to several previously reported illuminating formulations for the M126A1,⁶ M195,⁷ and M127A1⁸ hand-held signals. All three of these are currently in production and have been determined to be safe to handle. As detailed in Table 9,

Table 9. Sensitivity Data of Smoke Formulations Compared to Illuminating Compositions

formulation	impact (J)	friction (N)	ESD ^a (J)
M126A1 ⁵	8.8	80	>0.25
M195 ⁶	6.9	120	>0.25
M127A1 ⁷	11.3	>360	>0.25
F	17.2	>360	>0.25

^aESD = electrostatic discharge.

formulation F exhibited lower sensitivity to impact and friction and similar sensitivity to electrostatic discharge (ESD) relative to the illuminating formulations. Also noteworthy is that no sparks or reports were observed during any of the sensitivity trials for formulation F; instead, a positive sign for ignition was identified as the odor of caramelized sugar or darkening of the sample.

CONCLUSIONS

In summary, we have developed a system-ready yellow smoke formulation containing only environmentally benign solid ingredients that do not pose product life cycle management risks (i.e., long-term degradation or supply chain limitations). This formulation is expected to transition well to a manufacturing environment because it is relatively insensitive to physical ignition stimuli and does not require solvent-based (liquid) binders. In addition, the cardboard tube into which this smoke formulation is encased is an uncommon configuration³⁴ for colored smokes because such formulations are more commonly encased in steel³⁵ or plastic³⁶ containers. The cardboard tube configuration is advantageous because it is biodegradable, inexpensive, lightweight, rust proof, and cannot be reclaimed and repurposed by an enemy to effect collateral damage.

ASSOCIATED CONTENT

S Supporting Information

Particle size analyses for potassium chlorate (Table S1 and Figure S1), sugar (Table S2 and Figure S2), and Solvent Yellow 33 (Table S3 and Figure S3). Powder XRD pattern for hydromagnesite (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Professor Dennis P. Curran on the occasion of his 60th birthday.

ABBREVIATIONS

ARDEC = Armament Research, Development, and Engineering Center; EQT = Environmental Quality Technology; EPA = Environmental Protection Agency; ESD = electrostatic discharge; HHS = hand-held signal; IARC = International Agency for Research on Cancer; NATO = North Atlantic Treaty Organization; NC = nitrocellulose; OEP = Ordnance Environmental Program; RDECOM = Research, Development, and Engineering Command; STANAG = standardization agreement; U.S. = United States; VAAR = vinyl alcohol acetate resin; XRD = X-ray diffraction

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-Supporting Information for-

Prototype Scale Development of an Environmentally Benign Yellow Smoke Hand Held Signal Formulation Based on Solvent Yellow 33

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Particle size analysis of potassium chlorate (KClO_3).

Table S1: Circle equivalent (CE) diameter (number-based) data for KClO_3

	CE mean (microns)	CE STDEV (microns)	D[n, 0.1] ^a (microns)	D[n, 0.5] ^b (microns)	D[n, 0.9] ^c (microns)
KClO_3	25.80	25.09	2.24	6.40	38.45

^aD[n, 0.1] = Maximum diameter of 10% of the population.

^bD[n, 0.5] = Maximum diameter of 50% of the population.

^cD[n, 0.9] = Maximum diameter of 90% of the population.

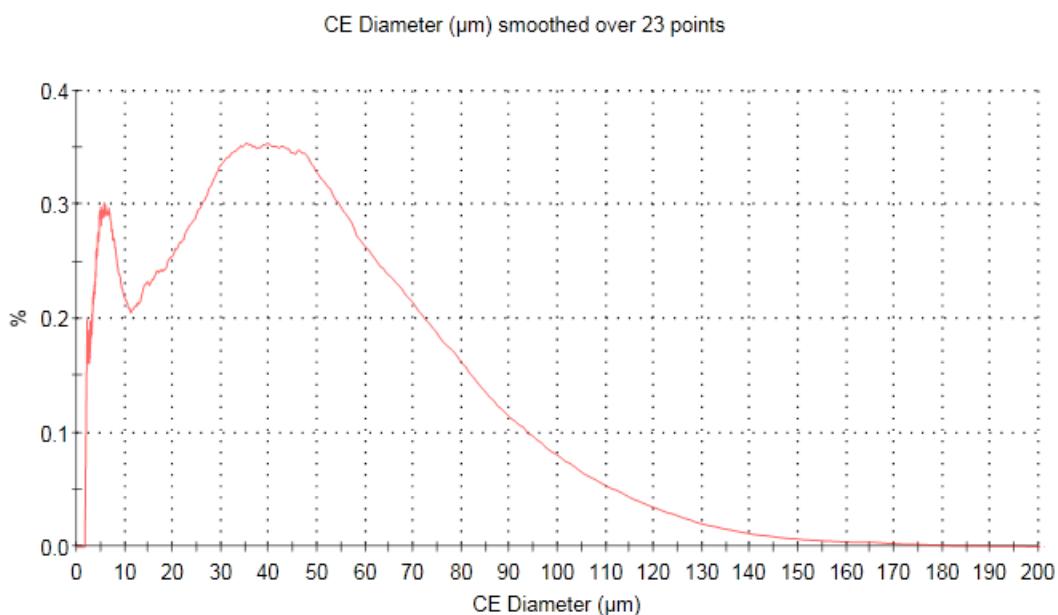


Figure S1: CE number-based particle size distribution plot for KClO_3 .

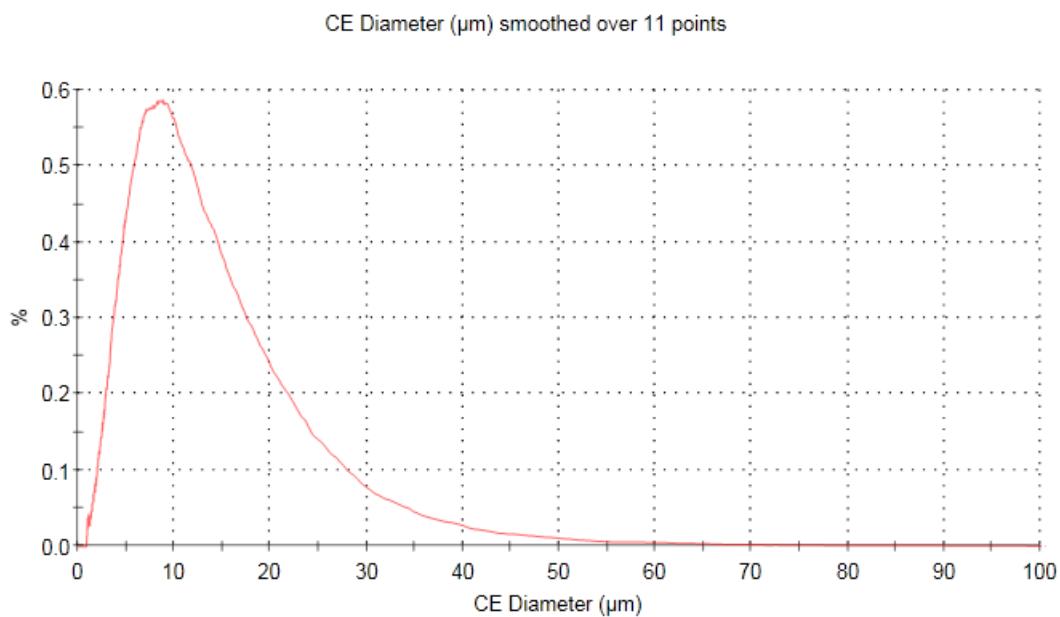
Particle size analysis of sugar (sucrose).**Table S2:** Circle equivalent (CE) diameter (number-based) data for sucrose

	CE mean (microns)	CE STDEV (microns)	D[n, 0.1] ^a	D[n, 0.5] ^b	D[n, 0.9] ^c
Sucrose	9.90	7.49	3.09	7.95	18.65

^aD[n, 0.1] = Maximum diameter of 10% of the population.

^bD[n, 0.5] = Maximum diameter of 50% of the population.

^cD[n, 0.9] = Maximum diameter of 90% of the population.

**Figure S2:** CE number-based particle size distribution plot for sucrose.

Particle size analysis of solvent yellow 33 (SY33).

Table S3: Circle equivalent (CE) diameter (number-based) data for SY33.

	CE mean (microns)	CE STDEV (microns)	D[n, 0.1] ^a (microns)	D[n, 0.5] ^b (microns)	D[n, 0.9] ^c (microns)
SY33	6.00	6.16	1.41	4.46	11.06

^aD[n, 0.1] = Maximum diameter of 10% of the population.

^bD[n, 0.5] = Maximum diameter of 50% of the population.

^cD[n, 0.9] = Maximum diameter of 90% of the population.

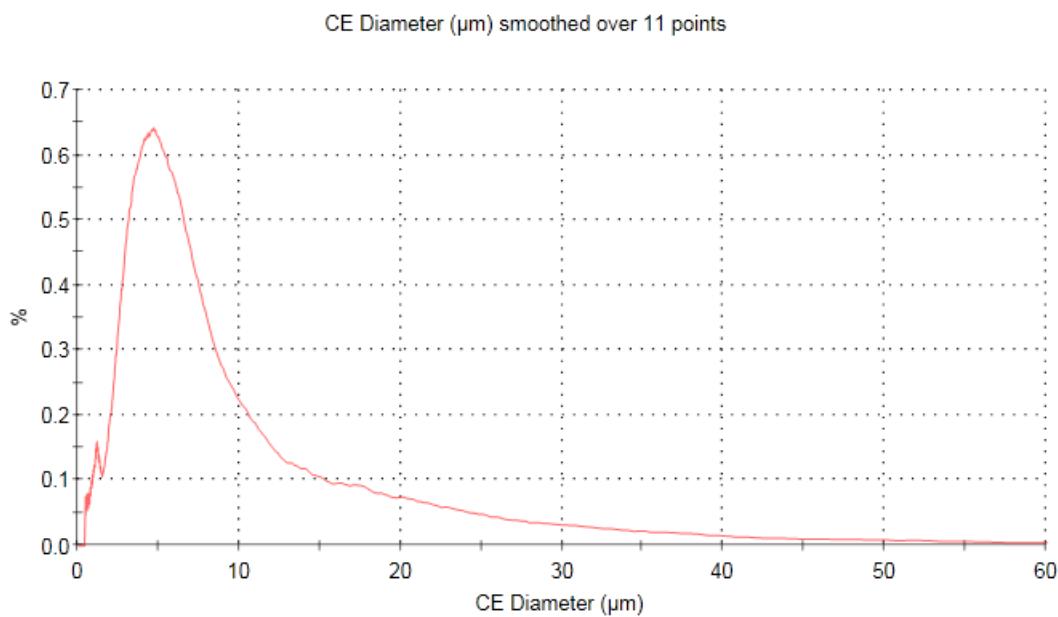


Figure S3: CE number-based particle size distribution plot for SY33.

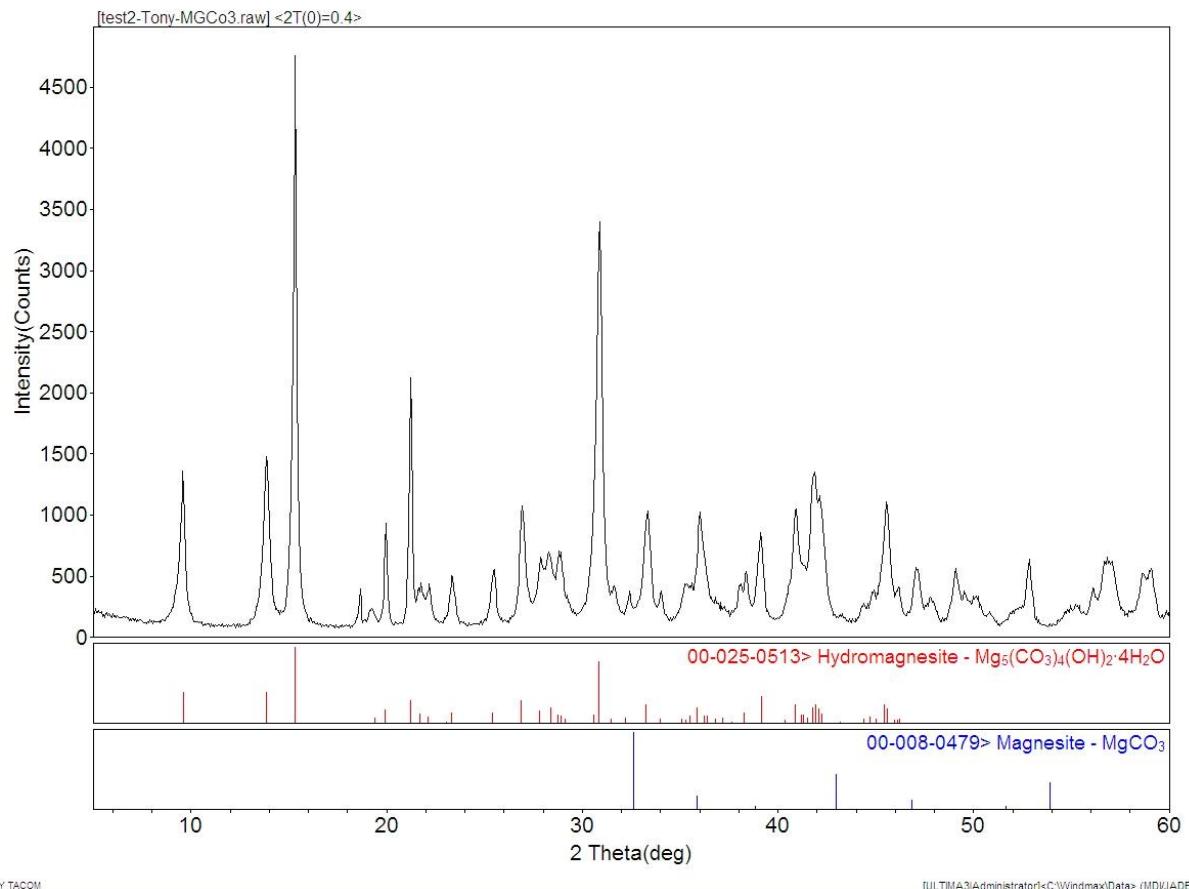


Figure S4: Powder X-ray diffraction pattern of our sample of hydromagnesite (top) compared to library database patterns for hydromagnesite (middle) and magnesite (bottom).